

VAN LONDON

Est. 1961



pHoenix Co.



Silver or Sulfid Ion Selective Electrode



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GENERAL INSTRUCTIONS

Introduction

The Van London-pHoenix Silver/Sulfide Ion Electrode is used to measure silver or sulfide ions in aqueous solutions. The two ions are virtually never present in solution together, due to the extreme insolubility of silver / sulfide. Indirect measurements of cyanide or measurements of halide ions by titration may be done with this electrode.

Required Equipment

1. An ion meter
2. Silver Sulfide Ion Sensing Electrode
3. Polishing Paper to polish dirty or etched Silver Sulfide electrode crystals.
4. Plastic syringe, pipets, volumetric flasks, 150 ml beakers

Required Solutions

1. Deionized or distilled water for solution preparation. Water used in the preparation of sulfide standards and of SAOB should also be de-aerated.

For Silver:

2. Van London-pHoenix Ionic Strength Adjuster (ISA), Cat. No. AGSIS01.
3. Van London-pHoenix Silver Standard, 1000 ppm as Ag^+ , Cat. No. AGSAS02.

For Sulfide:

2. Van London-pHoenix Sulfide Anti-Oxidant Buffer (SAOB) kit. This buffer must be used fresh and will range in color from clear to yellow-brown. It has become oxidized when it turns dark brown and should then be discarded. Store fresh SAOB in a tightly stoppered bottle. To prepare SAOB from your own stock, fill a 1 liter volumetric flask with about 500 mL of distilled, deaerated water, 200 mL of 10M NaOH, 35 grams of ascorbic acid, and 67 grams of disodium EDTA. Swirl the mixture until the solids dissolve and fill to the mark with distilled, deaerated water.
3. Sulfide Standard. To prepare a stock solution of saturated sodium sulfide, add about 100 grams of reagent grade $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ to 100 mL of distilled, deaerated water. Shake well and let stand overnight, storing in a tightly stoppered bottle in a hood.

Prepare a weekly sulfide standard by adding 500 mL SAOB to a 1 liter volumetric flask, pipetting 10 mL of the stock solution into the flask, and diluting to the mark with distilled, deaerated water.

The exact concentration, C, can be determined by titrating 10 mL of the standard with 0.1M lead perchlorate. Use the silver/sulfide ion electrode (and the reference electrode) to indicate the endpoint.

The calculation is as follows:

$$C = 3206(V_t/V_s)$$

where: C = concentration as ppm sulfide
 V_t = volume of titrant at endpoint
 V_s = volume of standard used (10 mL)

Prepare other standards each day by serial dilution of the weekly standard. To do a ten-fold dilution, accurately measure 10 mL of the standard and add it to a 100-mL volumetric flask. Add 45 mL of SAOB and dilute to the mark with distilled, de-aerated water.

4. Silver Sulfide Electrode Reference Fill Solution, Cat.# R001015.

GENERAL PREPARATION

Electrode Preparation

Remove the rubber cap covering the electrode tip and the rubber insert covering the filling hole of the reference electrode. Fill the combination electrode with the filling solution shipped with the electrode to a level just below the fill hole. No preparation is required with a sealed reference electrode. Connect the electrode to the proper terminals of the meter as recommended by the meter manufacturer. Store the black shipping cap for later use.

Electrode Slope Check (for Ion meters which display mV)

Using Silver standards:

1. To a clean, dry, 150 ml beaker, add 100 ml of distilled water and 2 ml of ISA. After assuring that the meter is in the millivolt mode, lower the electrode tip into the solution. Stir moderately. Remove air bubbles on the dark gray membrane by redipping probe.
2. Using a pipet, add 1 ml of 1000 ppm Silver standard into the solution. Stir moderately. After 1 minute, record the mV reading.
3. Using a pipet, add 10 ml of the 1000 ppm Silver standard to the beaker. Stir moderately. After 1 minute, record the mV reading.
4. Determine the difference between the two readings. The electrode is operating correctly if a slope difference of 54-59 mV is found, assuming the solution temperature is 25°C. Slope is defined as the change in mV observed when the concentration changes by a factor of 10.

Using Sulfide stock solutions:

1. To a 150-mL beaker, add 50 mL of distilled water and 50 mL of SAOB solution. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tips into the solution.
2. Using a pipet, add 1 mL of weekly standard sulfide solution to the beaker. When the reading has stabilized, record the millivolt reading.
3. Using a pipet, add 10 mL of weekly standard sulfide used above to the beaker. When the reading has stabilized, record the millivolt reading.
4. Determine the difference between the two readings. The electrode is operating correctly if a slope difference of 22-28 mV is found, assuming the solution temperature is 25°C. Slope is defined as the change in mV observed when the concentration changes by a factor of 10.

Measurement using an Ion Meter (in the Concentration Mode)

Using Silver standards:

1. By serial dilution of the 1000 ppm Silver Sulfide standard, prepare two Silver Sulfide standards whose concentration is near the expected sample concentration. (e.g 10 ppm and 100 ppm) For example, to make a 100 ppm standard, pipet 10 ml of the 1000 ppm standard into a 100 ml volumetric flask and dilute to volume with deionized water. Next to make a 10 ppm standard, pipet 10 ml of the newly-made 100 ppm standard into a 100 ml volumetric flask and dilute to volume with deionized water. A 1 ppm standard is made by further dilution of the 10 ppm standard. Measure out 100 ml of each standard into individual 150 ml beakers.
2. Assure that the meter is in the concentration mode and set for a 2-point calibration.
3. Lower the electrode tip into the least concentrated solution. Begin stirring at a constant rate. Add 2 ml of ISA to the solution and continue stirring.
4. After 1 minute, adjust the meter to the concentration of the more dilute Silver Sulfide standard and fix the value in the memory according to the meter manufacturer's instructions.
5. Rinse the electrode tip with distilled water and blot dry.
6. Lower the electrode tip into the more concentrated solution. Begin stirring at a constant rate. Add 2 ml of ISA to the solution and continue stirring.

7. After 1 minute, adjust the meter to the concentration of the more concentrated Silver Sulfide standard and fix the value in the memory according to the meter manufacturer's instructions.
8. Add 100 ml of the sample and 10 ml of ISA in a 150 ml beaker. Lower the electrode tip into the solution. Begin stirring at a constant rate. Ensure that the meter is in sample mode.
9. After 1 minute, read the concentration directly from the meter display.
10. The electrode should be re-calibrated every 2-3 hours. Simply repeat Steps 2-7 above.

Using Sulfide stock solutions:

1. By serial dilution of the weekly standard Sulfide solution, prepare two Sulfide standards whose concentration is near the expected sample concentration. (e.g 10 ppm and 100 ppm) For example, to make a 100 ppm standard, pipet 10 ml of the 1000 ppm standard into a 100 ml volumetric flask, add 50 ml SAOB and dilute to volume with deionized water. Next to make a 10 ppm standard, pipet 10 ml of the newly-made 100 ppm standard into a 100 ml volumetric flask, add 50 ml of SAOB and dilute to volume with deionized water. A 1 ppm standard is made by further dilution of the 10 ppm standard. Measure out 50 ml of each standard into individual 150 ml beakers.
2. Assure that the meter is in the concentration mode and set for a 2-point calibration.
3. Lower the electrode tip into the least concentrated solution. Begin stirring at a constant rate.
4. After 1 minute, adjust the meter to the concentration of the more dilute Sulfide standard and fix the value in the memory according to the meter manufacturer's instructions.
5. Rinse the electrode tip with distilled water and blot dry.
6. Lower the electrode tip into the more concentrated solution. Begin stirring at a constant rate.
7. After 1 minute, adjust the meter to the concentration of the more concentrated Sulfide standard and fix the value in the memory according to the meter manufacturer's instructions.
8. Add 50 ml of the sample and 50 ml of ISA in a 150 ml beaker. Lower the electrode tip into the solution. Begin stirring at a constant rate. Ensure that the meter is in sample mode.
9. After 1 minute, read the concentration directly from the meter display.
10. The electrode should be re-calibrated every 2-3 hours. Simply repeat Steps 2-7 above.

Measuring Hints

As Silver Sulfide electrodes are used or stored for long periods, they will experience some deterioration in performance and slope errors will increase. By using the meter's calibration controls this error can be corrected. If an electrode is able to be calibrated and is stable and responsive, it is still a functional electrode and may be used in service even though it no longer meets "new" electrode specifications.

All samples and standards should be at the same temperature for precise measurement. A difference of 1°C in temperature will result in approximately a 2% error.

Always rinse the electrode with distilled water and blot dry between measurements. Use a clean, dry tissue to prevent cross-contamination.

Constant, but not violent, stirring is necessary for accurate measurement.

Check the electrode for air bubbles adhering to the membrane surface after immersion in solution. Agitate the electrode gently to remove the air bubbles.

All silver samples and silver standards should be stored away from light.

Always dilute sulfide samples with SAOB (1:1) when they are collected.

A slow or sluggish electrode response may indicate surface contamination of the membrane. Use a moistened polishing strip to lightly scrub the membrane surface, then soak in deionized water for five minutes to restore proper performance.

Use fresh standards for calibration. Re-calibrate every few hours for routine measurement.

All samples must be aqueous and not contain organics which can dissolve the epoxy electrode body and/or the cement bonding the sensing crystal to the electrode body. Infrequent measurements in solutions containing methanol, ethanol, benzene, and acetonitrile are permitted. Highly polar solvents slowly attack the electrode. Please check with Van London-pHoenix Electrode Company before using the electrode in other organic solvents.

Samples containing sulfide must be buffered with SAOB to convert HS^{-1} and H_2S to S^{-2} .

Samples containing silver must be below pH 8 to avoid reaction with OH^{-1} . Silver samples should be acidified with 1M HNO_3 , if necessary.

Mercury cannot be present in silver samples. Since HgS and Hg_2S are insoluble, no mercury will be present in sulfide samples. Other interferences should be absent. If they are present, use the procedures found in the **Interferences** and **Electrode Response** sections to remove them.

ELECTRODE CHARACTERISTICS

Reproducibility

Electrode measurements reproducible to $\pm 2\%$ can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuation, drift, and noise limit reproducibility.

Interferences

A surface layer of silver metal may be formed by strongly reducing solutions. A layer of silver salt may be deposited on the membrane if high levels of ions forming very insoluble salts are present in the sample. Performance may be restored by polishing. See the section **Electrode Response** for proper polishing procedure.

All silver samples must be free of mercury. Sulfide samples will not have mercury present due to the extreme insolubility of HgS and Hg_2S . Biological samples and protein in food interferes with silver measurements, but the protein interference can be removed by acidifying to pH 2-3 with 1M HNO_3 .

Complexation

Total concentration (C_t) whether sulfide or silver ions, consists of free ions (C_f) and complexed or bound ions (C_c) in solution:

$$C_t = C_f + C_c$$

Since the electrode only responds to free ions, any complexing agent in the solution reduces the measured concentration of ions.

Silver ions complex with many species, notably cyanide, thiosulfate, ammonia and chelants such as EDTA.

Sulfide ions form complexes with hydrogen ions (HS^{-1} and H_2S). Sulfide ions also form soluble complexes with elemental sulfur (S_2^{-2} , S_3^{-2} , S_4^{-2} , etc.) and tin, arsenic, and antimony ions.

Temperature Influences

The electrode response will shift and change slope with change in temperature. Standards and samples should be at the same temperature. A 2% error results with a 1°C temperature change for a 10 ppm solution.

The electrode can be used at temperatures from 0° - 80°C. Room temperature measurements are recommended, since measurements at temperatures quite different from room temperature may require equilibrium times up to one hour.

Electrode Response

Plotting the electrode mV potential against the silver concentration results in a straight line with a slope of about 57 mV between 10 ppm and 100 ppm at 25°C. The sulfide ion also gives a straight line when the electrode mV potential is plotted against the sulfide concentration, but the slope is about 26 mV between 10 ppm and 100 ppm at 25°C.

For concentrations above 10 ppm Ag^+ or S^{2-} , the electrode exhibits good time response (95% of total mV reading in one minute or less). Response times are longer below this value.

A drifting potential reading or a decrease in electrode slope may mean that the electrode membrane needs polishing.

To polish the membrane:

1. If using polishing paper, cut off a 1-2" piece and place it face up on the lab bench.
2. Put a few drops of distilled or deionized water in the center of the paper.
3. Holding the paper (cotton) steady with one hand, bring the membrane of the electrode down perpendicular to the paper and, with a slight swirling motion, gently polish the tip of the electrode against the surface of the polishing paper (cotton) for a few seconds.
4. Rinse the electrode surface with distilled or deionized water and soak the electrode tip in standard solution for about five minutes before use.

Limits of Detection

Silver levels from 0.1 ppm to saturated and sulfide levels from 0.003 ppm to saturated can be measured with the Silver Sulfide electrode.

The electrodes respond to Silver or Sulfide in the sample as well as to ions dissolved from the membrane at low levels. The electrode membrane shows a very slight water solubility. The detection limit of the electrode is determined by this factor. Plastic lab-ware must be used and the beakers must be covered with Parafilm for low level Silver or Sulfide determinations or Silver or Sulfide will be lost. Allow a longer stabilization time before taking the meter reading for best results.

pH Effects

Silver reacts with hydroxide ions to form a precipitate of Ag_2O , in ammonia-free basic solutions. By keeping all solutions slightly acidic, this can be avoided. Adjust the pH of silver solutions below 8, if necessary, with 1M HNO_3 .

Bisulfide ion (HS^-) and hydrogen sulfide (H_2S) result when hydrogen ion complexes sulfide ion. Larger amounts of sulfide ion are complexed as the pH is lowered. The use of SAOB in all samples containing sulfide maintains a fixed level of S^{2-} ions, since the free sulfide ion (S^{2-}) exists in only very basic solutions. In the acid range, sulfide is chiefly in the form of H_2S , while in the pH range 6-12, almost all the sulfide is in the HS^- form.

Electrode Life

The Silver Sulfide electrode will last one year in normal laboratory use. On-line measurements might shorten operational lifetime to several months. In time, the response time will increase and the calibration slope will decrease to the point calibration is difficult and electrode replacement is required.

Since Silver Sulfide electrodes have a limited shelf life, it is important to have a backup electrode which is in working condition when required.

Electrode Storage

The Silver Sulfide electrode may be stored for short periods of time in 10 ppm Silver solution with ISA added or Sulfide solution with SAOB added. For longer storage (longer than two weeks), rinse and dry the sensing pellet and cover the membrane

tip with any protective cap shipped with the electrode. The reference portion of the combination electrode (or the outer chamber of the reference electrode) should be drained of filling solution, if refillable, and the rubber insert placed over the filling hole.

TROUBLESHOOTING HINTS

*Remember to remove the black protective shipping cap on the bottom of the electrode and expose the fill hole underneath the electrode cap. Fill the electrode with the Reference Filling Solution shipped with the electrode to a level just below the fill hole.

<u>Symptom</u>	<u>Possible Causes</u>	<u>Next Step</u>
Out of Range Reading	defective meter	check meter with shorting strap (see meter instruction manual)
	defective electrode	check electrode operation
	electrode not plugged in properly	unplug electrode from meter and reseal
	electrode reference chamber not filled	fill reference chamber as instructed in <u>Electrode Preparation</u>
	air bubble on membrane	remove air bubble by re-dipping electrode
Noisy or Unstable Reading (readings continuously or randomly changing.)	electrode not in solution	put electrode in solution
	insufficient reference filling solution	fill outer body of electrode with proper amount of reference filling solution
	defective meter	check meter with shorting strap (see meter instruction manual)
	defective electrode	check electrode operation
	air bubble on membrane	remove air bubble by re-dipping electrode
Drift (reading slowly changing in one direction)	meter or stirrer improperly grounded	check meter and stirrer for grounding
	electrode exposed to interferences	soak electrode in Silver or Sulfide stand with ISA
	incorrect reference filling solution	refill outer body of electrode using filling solution shipped with electrode
	total sample level of dissolved species above 1M	dilute sample
	membrane failure(wet, perforation, discoloration)	replace electrode
	samples and standards at different temperatures	allow samples and standards to come to same temperature before measurement

Low Slope or No Slope	standards contaminated or incorrectly made	prepare fresh standards
	ISA not used	use recommended ISA
	standard used as ISA	use ISA
	membrane failure(wet, perforation, discoloration)	replace electrode
"Incorrect Answer" but calibration curve is good)	incorrect standards	prepare fresh standards
	wrong units used	apply correct conversion factor: $10^{-3}\text{M} = 107.8 \text{ ppm as Ag}^{+1} = 32 \text{ ppm as S}^{-2}$
	ISA added to standards and not samples	add same proportions of ISA to standards and samples
	sample carryover	rinse electrodes thoroughly between samples

SPECIFICATIONS

Concentration Range:	108,000 to 0.1 ppm Ag^{+1} 32,000 to 0.003 ppm S^{-2}
pH Range:	2 to 12
Slope:	53 – 59 mV Ag^{+1} between 10 ppm and 100 ppm at 25°C 23 – 28 mV S^{-2} between 10 ppm and 100 ppm at 25°C
Temperature Range:	0° to 80°C
Interferences:	Hg^{+2} , Hg^{+1}
Reproducibility:	$\pm 2\%$
Size:	110 mm length 12 mm diameter
Storage:	store electrode in Silver standard with ISA added of Sulfide standard with SAOB added

ELECTRODE THEORY

Electrode Operation

The Silver/Sulfide Ion Electrode is composed of a silver sulfide crystal membrane bonded into an epoxy or glass body. When an electrode potential develops across the membrane, the membrane is in contact with a solution containing sulfide or silver ions and is capable of measuring free sulfide or silver ions. This electrode potential is measured against a constant reference potential, using a pH/mV meter or an ion meter. The level of sulfide or silver ions, corresponding to the measured potential, is described by the Nernst equation:

$$E = E_0 + S \log X$$

where:	E	= measured electrode potential
	E_0	= reference potential (a constant)
	S	= electrode slope (-26 mV for sulfide; +57 mV for silver)
	X	= level of sulfide or silver in solution

The activity, X , represents the effective concentration of the ions in solution. The activity is related to the free ion concentration, C_f , by the activity coefficient, γ , by:

$$X = \gamma C_f$$

Activity coefficients vary, depending on total ionic strength, I , defined as:

$$I = 1/2 \sum C_x Z_x^2$$

where: C_x = concentration of ion X
 Z_x = charge of ion X
 Σ = sum of all of the types of ions in the solution.

In the case of high and constant ionic strength relative to the sensed ion concentration, the activity coefficient, γ , is constant and the activity, X , is directly proportional to the concentration.